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CARS study of linewidths of the Q-branch of hydrogen molecules at high temperatures in a pulsed high-pressure $H_2 - O_2$ combustion chamber

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Abstract. **The results of measurements of individual line widths of the Q-branch of a hydrogen molecule and the corresponding coefficients of broadening caused by collisions with water molecules at $T = 2700$ K in a repetitively pulsed high-pressure (50 – 200 atm) hydrogen-oxygen combustion chamber are presented. CARS spectra of individual Q_1–Q_7 hydrogen lines, pressure pulses, and the broadband CARS spectra of the entire Q-branch of hydrogen are recorded simultaneously during a single laser pulse. The shape of line profiles was analysed using a Fabry–Perot interferometer. The temperature in the volume being probed was determined from the 'broadband' CARS spectra. The entire body of the experimental results gives information on the spectral linewidths, temperature and pressure in the combustion chamber during CARS probing.**

Keywords: coherent anti-Stokes Raman scattering (CARS), collision broadening coefficients, Fabry–Perot interferometer, combustion thermometry, hydrogen–oxygen burning.

1. Introduction

One of the most important tasks in diagnostics of flames in various types of combustion chambers is to determine the spatial distributions of temperature and concentration of various components of the gaseous mixture [1, 2]. The fitting procedure, in which the experimental spectrum of the 'probe' molecule is compared with the model spectra calculated at known temperatures, is used for temperature measurement by CARS spectroscopy. A comparison of the best fit of the experimental spectrum with one of the theoretical spectra leads to the conclusion that the temperatures corresponding to these spectra are equal. The precision with which the temperature is measured in this procedure depends on the reliability and comprehensiveness of the knowledge about molecular spectroscopy constants, coefficients of collision broadening of spectral lines taking into account their temperature dependence and concentrations of molecules colliding with the 'probe' molecule.

It is convenient to use hydrogen molecules as 'probe' molecules for studying hydrogenous flames since the molecular constants, Raman scattering cross sections and self-broadening coefficients of hydrogen at temperatures below 1000 K are all well known [3, 4]. However, it is still quite difficult to obtain data about the broadening of transitions in collisions of hydrogen molecules with one another or different molecules at high temperatures (higher than 1000 K). For example, the broadening coefficients of spectral lines of hydrogen in collisions of hydrogen molecules with N_2, H_2 and H_2O molecules were measured in [5, 6] at temperatures up to 1800 K. Measurements were made in a heated high-pressure cell under steady-state conditions. It was mentioned in [6] that high chemical activity of water vapour molecules is the principal factor determining the upper limit of temperature in the cell.

Direct measurements in a hydrogen–oxygen combustion chamber with controllable parameters, in which higher temperatures (up to 3000 K) can be attained under a continuous renewal of the medium, may serve as an alternative to measurements in a heated cell under steady-state conditions. While planning such experiments, we were guided by the results of earlier measurements of the broadening coefficient γ of lines of hydrogen molecules in their collisions with H_2 molecules ($\gamma_1 = 6 \times 10^{-3}$ cm^{-1}amagat^{-1} [4]) and with H_2O molecules ($\gamma_2 = 22 \times 10^{-3}$ cm^{-1}amagat^{-1} [5, 6]), which were obtained at temperatures not exceeding 1800 K. We also used the results of model calculation performed by the authors of [7] who used them to extrapolate the experimental results obtained in [5, 6] to the temperature range up to 3000 K. According to their estimates, the broadening coefficients of spectral lines increase with temperature ($\gamma_2 \sim 70 \times 10^{-3}$ cm^{-1}amagat^{-1}) and a pronounced dependence of the linewidths on the rotational quantum number J (J-dependence) is preserved. The Doppler width Γ_D of the Q-branch lines of hydrogen molecules at 2500 – 3000 K is about 115×10^{-3} cm^{-1}. By using these data and taking into account the fact that the products of combustion of the $H_2 - O_2$ mixture contain at such temperatures about 80 % of water vapour [8], it can be concluded that for a density of water vapour exceeding 1 amagat, the Q-branch lines will be homogeneously broadened, mainly due to collisions of hydrogen molecules with water molecules.

Thus, it is sufficient to vary the density of water vapour in the range 1 – 10 amagat for measuring the broadening

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coefficients. The pressure in the combustion chamber in this case is $\sim 100-200$ atm. Since such conditions are hard to realise technically in the continuous combustion regime, we designed a high-pressure hydrogen–oxygen combustion chamber (repetitively pulsed chamber) intended for operation in the repetitively pulsed regime (up to 10 Hz). This device with a small volume (~ 2 cm^3) of the chamber and an initial pressure of the working mixture up to 20 atm makes it possible to produce a high pressure (~ 200 atm) of the combustion products at temperatures up to 3000 K. Such a construction eliminates problems connected with the chemical activity of the combustion products and the overheating of the device, and allows measurements continuously for several hours with a low consumption of fuel and oxidant.

In this work, we present the results of measurement of the individual linewidths of the Q-branch of hydrogen molecules caused by collisions of hydrogen molecules with water molecules at $T = 2700$ K. These results were obtained with the help of a high-pressure repetitively pulsed hydrogen–oxygen combustion chamber with controlled pressure and temperature.

In the pulsed regime and under transient conditions in the combustion chamber, all measurements must be made during the period of a single laser pulse synchronised with the combustion cycle. A diagnostic system with three recording channels was developed for such measurements. The first channel was used for measuring the widths of individual CARS lines of the Q-branch of hydrogen molecules and employed a pulsed 'narrowband' CARS spectrometer tuned to a selected line. A Fabry–Perot interferometer was used to analyse the line shape. (Such an approach was used recently for studying the linewidths of deuterium molecules in a shock tube [9].) The second channel was used to measure the temperature in the combustion chamber. For this purpose, a 'broadband' CARS spectrometer was employed for a simultaneous recording of all spectral lines of the Q-branch of hydrogen molecules and the ν_1 vibrational spectrum of the Q-branch of water molecules. Spectral data in both channels were detected with multichannel optical analysers. The time dependence of the pressure in the combustion chamber, laser pulse during CARS probing, and the data on fuel and oxidiser consumption were recorded in the third channel. Thus, a single cycle of the pulse combustion chamber operation provides information about the line shape, temperature and pressure in the volume under study during CARS probing.

2. Experimental setup

2.1 Pulsed burner

The pulsed burner was constructed as follows (Fig. 1). A stainless steel cylinder of diameter 15 mm and length 10 mm was used as the combustion chamber. A spark plug and a pressure gauge are mounted at the top and bottom of the cylinder. Gaseous H_2 and O_2 are supplied to the combustion chamber through two main lines, each having an electromagnetic pulse valve, a check valve, regulators and input pressure and gas flow gauges, as well as a buffer reservoir of volume 2 L. The input pressure of each gas can be varied in the range 1–30 atm.

The cylindrical surface of the combustion chamber has two coaxial holes of diameter 1.4 mm that are always open. The cross section of these holes is much smaller than that of the main gas supply lines, so that at the initial stage of gas inflow, when the electromagnetic valves are open, the pressure in the combustion chamber is close to the gas

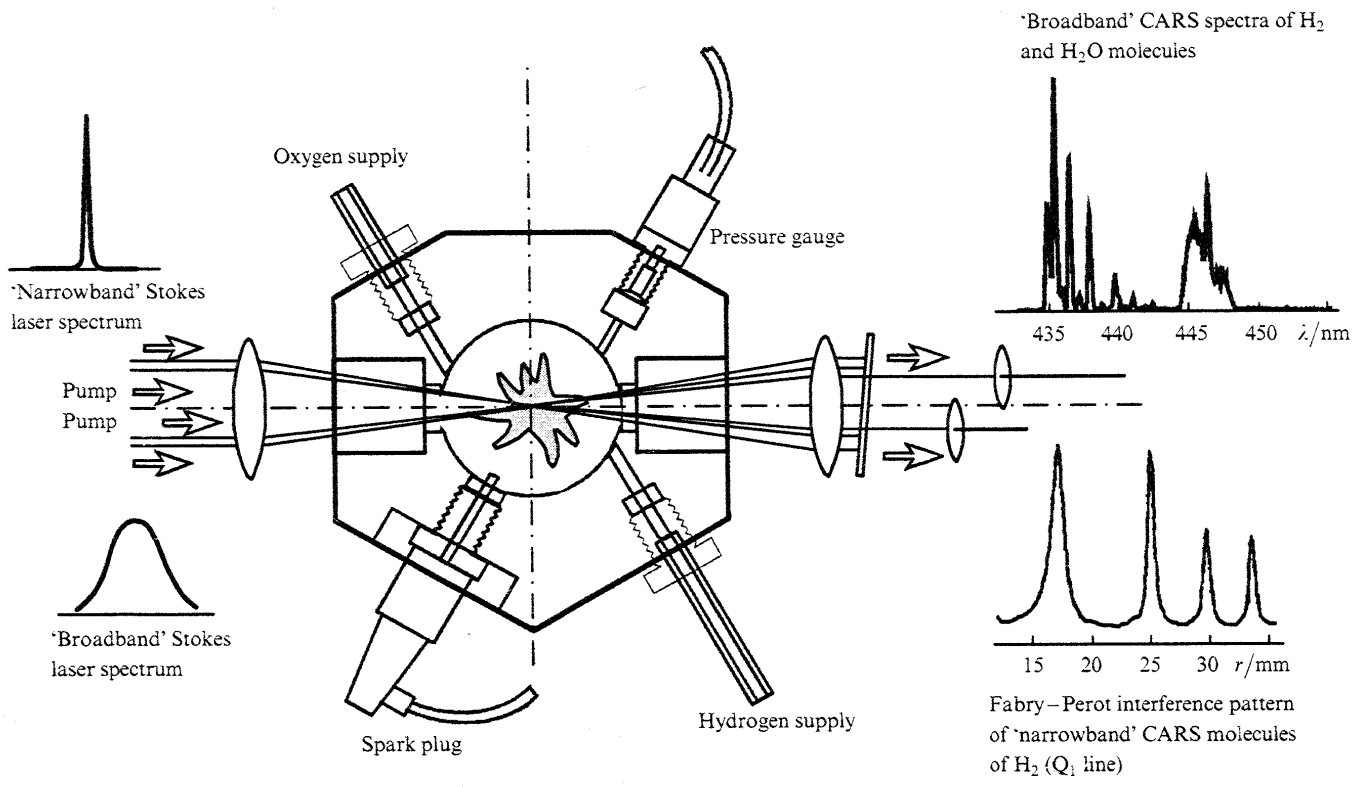

Figure 1. Scheme of three-channel probing of the pulsed high-pressure hydrogen–oxygen combustion chamber.

inflow pressure. After closure of the electromagnetic valves, the combustible mixture is ignited by the spark plug, burns away for a few microseconds, the temperature and pressure in the chamber increase by an order of magnitude compared to their initial values. Then, the combustion products flow out from the chamber to the surroundings for a few milliseconds through the outlet holes, thus providing a smooth lowering of pressure in the probed volume and cleaning of the chamber between two successive combustion cycles. The same holes are used for introducing and extracting light beams.

An electronic circuit controls the valves, generates the ignition pulse for the spark plug and provides a set of trigger pulses for synchronising the lasers and the data collection system. The electronic control unit makes it possible to vary independently the time in the range 10–100 ms for which any valve is open, the delay between the instants of their opening, as well as the spark pulse delay. For safety reasons, the mixture is ignited after both the valves have been closed.

An important parameter affecting the temperature and pressure attained in the chamber is the ratio of the initial concentrations of the fuel and the oxidant. This parameter is determined by measuring the volumetric flow rates of both components of the combustible mixture. The concentration ratio may be varied by changing the input pressure of each gas.

2.2 Lasers and the recording systems

The two CARS-probing channels differ in the spectral properties of the Stokes lasers used in them and the methods of recording and analysing the CARS spectra. As a pump source in CARS processes and Stokes lasers, we used second-harmonic radiation from a single-frequency (spectral width ~ 100 MHz) Infinity Nd^{3+} : YAG laser (Coherent Radiation). A 3-ns, 532-nm laser pulse has a typical energy of $100-120$ mJ, which is distributed as follows. The energy of pump waves in the CARS process is $10-15$ mJ per channel. Pumping of each Stokes laser requires an energy of 25 mJ. Both Stokes lasers use identical oscillator–amplifier schemes employing a solution of the organic dye pyridine in methanol.

The resonator of the Stokes laser oscillator in the first channel consists of an output mirror, a grazing-incidence diffraction grating, and a rear mirror. Radiation from the transversely pumped oscillator is amplified in a single-pass amplifier, which is also pumped transversely. The output energy of this laser is ~ 3 mJ for a radiation linewidth of ~ 5 cm^{-1}. On the one hand, such a spectral width is much larger than the width of any line in the Q-branch, while on the other hand, it is less than the frequency separation between adjacent lines in the spectrum. This allows us to record the entire profile of a chosen spectral line during a laser pulse. An LM-007 laser wavelength meter (ATOS GmbH) was used for tuning the Stokes laser to individual transitions of the Q-branch. The CARS spectrum in the first channel was analysed with a LOMO IT-28-30 Fabry–Perot interferometer (aluminium mirrors with a reflectance of 92% and a free spectral range of 0.5 cm^{-1}) by recording the interference pattern with a multichannel linear photodetector.

The oscillator of the Stokes laser in the second channel, which is used for measuring temperature, is a transversely pumped mode-free generator assembled as a double-pass amplifier with a single rear mirror. Radiation from the oscillator is amplified in a single-pass transversely pumped dye amplifier. It has an output energy of ~ 3 mJ for the linewidth exceeding 500 cm^{-1}, which makes it possible to record simultaneously the CARS spectra of the Q-branches of hydrogen and water. The CARS spectrum was recorded with an HR 460 Jobin–Ivon grating spectrograph (1200 lines mm^{-1} diffraction grating, focal length 460 mm) equipped with a multichannel linear photodetector.

To increase the spatial resolution, the 'planar CARS' geometry of laser beam interaction was used in each CARS channel. The pump beam and the Stokes beam are parallel to each other and separated by a distance of ~ 10 mm. As these beams are focused by a lens ($f = 300$ mm), they intersect in the focal region at a small angle, which prevents the CARS signal generation in the regions of the medium outside the volume being probed. Two pairs of CARS pump beams (from the first and second channels) also intersect in the probe volume at a small angle, which provides their spatial separation in channels for individual recording. In addition, laser pulses in the first channel are delayed by about 7 ns relative to the second-channel pulses to prevent mutual interference of channels.

The third channel is used for measuring pressure in the combustion chamber at the stages of inflow, burning and escape of products in each working cycle. These measurements are performed with a 6061B piezoelectric pressure gauge (Kistler) mounted in the wall of the combustion chamber. The signal from the gauge is amplified by a wideband charge amplifier. The dynamic range and the response time of the gauge make it possible to measure pressure during relatively slow stages of inflow and to check the rapid pressure changes at the stages of burning and escape. Before measurements, the pressure gauge was calibrated in the range 1–150 atm.

In the experiment, the signal from the pressure gauge amplifier was digitised by a two-channel analogue-to-digital converter (ADC) and was stored in the hard disc of a computer. The second ADC channel was used for digitising the signal from a fast photodiode which detected the laser pulse. Such a two-channel recording makes it possible to determine the pressure precisely at the instant of CARS probing of the combustion chamber. The delay generator was used for varying the time between the instants of mixture ignition and of the CARS probing. This makes it possible to carry out measurements at densities that vary with time due to escape of combustion products from the chamber through outlet holes.

3. Results and discussion

The experiment was performed as follows. The pressure and volumetric flow rates of H_2 and O_2 were preset. The burner operated with a repetition rate of 1 Hz. The wavelength of the 'narrowband' Stokes laser was tuned to the Raman frequency of one of the odd ($J = 1, 3, 5, 7$) lines of the Q-branch of hydrogen molecules, and the wavelength range of the 'broadband' laser was selected to cover the lines of the Q-branch of hydrogen molecules and the ν_1 band of water molecules. After setting the appropriate delay between the instants of ignition and probe laser pulses, about 50 files synchronised with ignition and with one another and containing data from three channels were recorded. After recording the data, the gas flow rate or the Stokes

wavelength in the first channel or the delay between ignition and probing were varied and measurements were repeated.

Preliminary analysis of the data obtained for identical initial inflow pressures and delays showed that the temperature and pressure at the end of burning in various cycles could differ by 30 %. In view of this, we adopted the following approach for data processing. At the first stage, the temperature was determined preliminarily by processing CARS spectra of the Q-branch of hydrogen molecules under the assumption that the spectral linewidths are independent of J. The absolute temperatures determined in this way show a systematic deviation from the correct values. However, these rough estimates of temperature are necessary for subsequent selection of data files for the working cycles of the combustion chamber, in which identical values of temperature and pressure were realised. The files chosen as a result of such a selection were used for subsequent averaging of data over $Q_1 - Q_7$ linewidths obtained in individual working cycles. At the second stage of processing, the data on linewidths and their J-dependences were used for approximating the CARS spectra and a correct evaluation of the gas temperature.

As a result of such a procedure, the values of temperature, linewidths, and their J-dependences, which are averaged over the selected sampling, are determined at a certain pressure. However, such data are required to measure the broadening coefficients and their temperature dependence for various pressures and temperatures. To study the dynamic range of these parameters, we analysed the operating conditions of the pulsed combustion chamber and determined optimal conditions for using the chamber to measure the linewidths.

The following circumstances should be taken into account. A satisfactory signal-to-noise ratio in the CARS channels requires a sufficient amount of hydrogen in the probe volume, which necessitates the use of enriched mixtures. However, the burner operation is not stable and steady in all regimes in this case. We determined experimentally the conditions for its stable operation in enriched mixtures and used these regimes in our investigations. The optimal regime for stable burner operation corresponds to a temperature of 2700 K for an excess oxidant factor $\alpha = 0.45$. Attempts to vary the temperature by changing the ratio of fuel and oxidant through an enrichment of the mixture allowed the temperature reduction from 2700 K to 2000 K. Therefore, within the framework of this study of high-temperature regimes, we measured the broadening coefficients only at temperatures 2700 ± 200 K.

For such a stoichiometry of the mixture, we measured the pressure in the combustion chamber at the stages of gas inflow, burning and escape of the combustion products from the chamber through the outlet holes that are always open. Figure 2 shows a typical time dependence of the pressure. The chamber is filled with the mixture during about 10 ms, and the steady-state pressure in the chamber can be set in the range 5–20 atm. After ignition, the pressure increases to 50–200 atm for a few microseconds. Then, due to the escape of the combustion products through the holes, the pressure in the chamber drops to the atmospheric pressure during a few milliseconds. The pulse-to-pulse fluctuations of the peak values of pressure do not exceed 10 %.

Temperature measurements in the chamber for a given stoichiometry of the mixture show that as the delay time

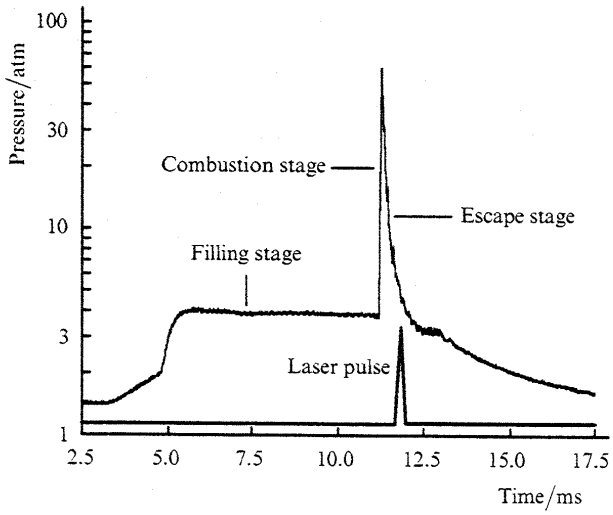

Figure 2. Time dependence of pressure in the chamber.

between ignition and probe varies in the range 30 – 180 μs, the temperature of the products in the combustion chamber remains almost unchanged (Fig. 3) and does not depend on the mixture pressure in the chamber. During this time, the pressure in the chamber drops to nearly half its value (see Figs 2, 3). Since the filling pressure can vary by a factor of four (5–20 atm), the total dynamic range of variation in the pressure of the combustion products at a constant temperature is eight. Thus, we conclude that the collision broadening of hydrogen lines by water molecules can be measured in this burner at a constant temperature at the water-vapour densities from 1 to 8 amagat.

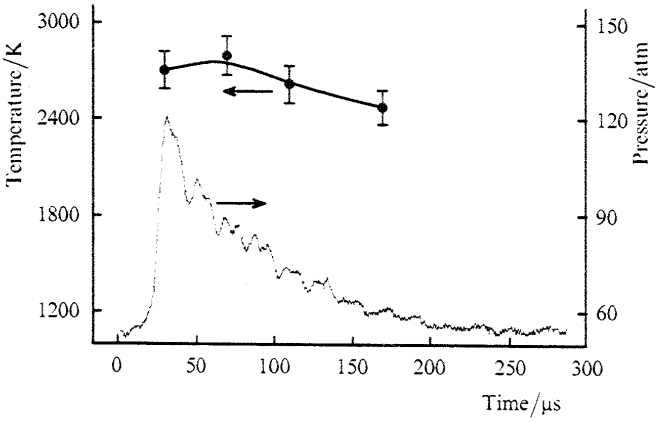

Figure 3. Time dependence of temperature and pressure in the combustion chamber at the stage of escape of combustion products.

The linewidths were measured by presenting the averaged Fabry–Perot interference patterns in the linearised radial-coordinate scale on which the interference fringes are equidistant. In this case, the profiles of interference fringes are described by a Lorentzian profile whose parameters, including the FWHM, were determined by fitting the spectral profiles by the method of least squares. Figure 4 shows linearised Fabry–Perot interference patterns for $J = 7$ and the results of their approximation by Lorentzian contours. The instrumental function was determined by illuminating the interferometer with CARS radiation

obtained in the cell containing hydrogen under a pressure of 1 atm at room temperature. Under these conditions (Dicke narrowing region), the Q_1 line of the CARS spectrum has the FWHM ~ 0.012 cm^{-1} [4]. Our measurements show that for an interferometer base of 1 cm, its finesse is 15 and the instrumental function has the FWHM 0.033 cm^{-1}. The measured instrumental function was taken into account during processing of the Fabry–Perot interference patterns.

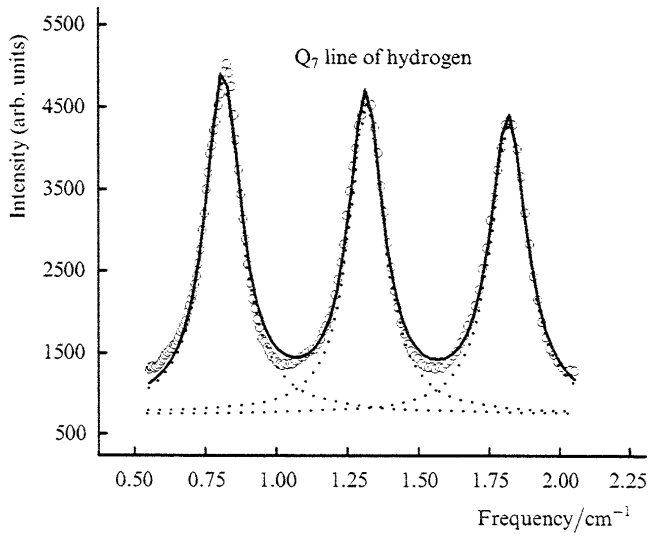

Figure 4. Linearised interference patterns of a 'narrowband' CARS channel for the Q_7 line. The circles correspond to the experiment while the dashed curves show the best fit of the interference fringes by Lorentzian profiles; the solid curve is the best-fit envelope of the interference pattern.

The linewidth measurements for odd values of J from 1 to 7 were made at 2700 K for three different pressure ranges (delays between ignition and probing). To determine the spectral-line broadening coefficients, the water-vapour density in the combustion chamber during probing should be known. We estimated it from the tables in [8] from the measured values of temperature, total pressure in the chamber, and the initial ratios of fuel and oxidants. Figure 5 shows the results of measurement of the linewidths of the Q-

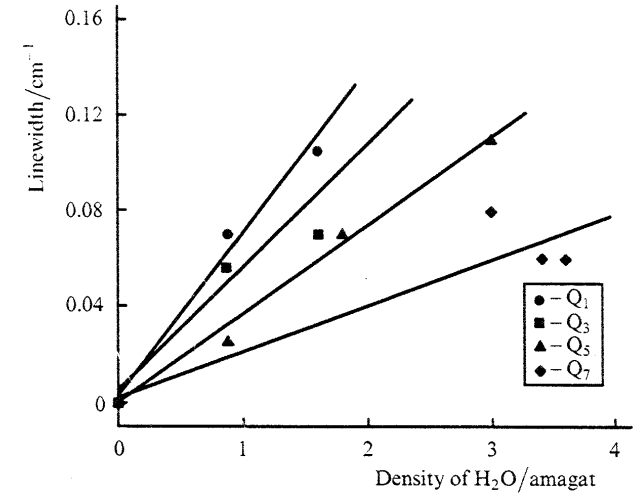

Figure 5. Dependence of the FWHM of the Q-branch lines of hydrogen molecules on the water-vapour density at 2700 K.

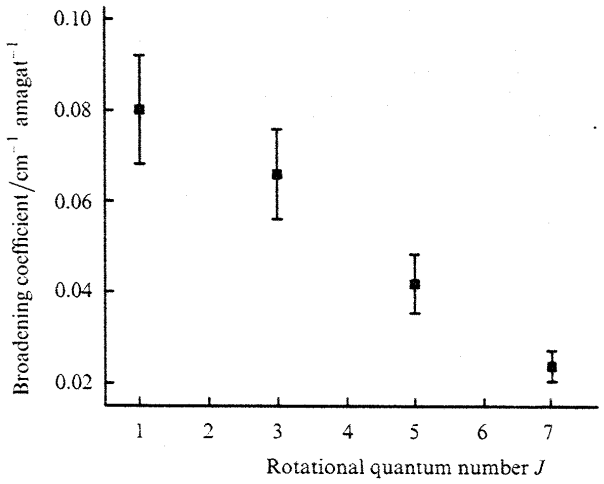

Figure 6. Collision broadening coefficients obtained at 2700 K for the Q-branch lines of hydrogen molecules with different rotational quantum numbers J.

branch for hydrogen molecules at $J = 1, 3, 5, 7$ depending on the water-vapour density. The broadening coefficients obtained from these data are shown in Fig. 6. Note that our results are in good agreement with the theoretical extrapolation to 3000 K of the data on the broadening coefficients [7] obtained experimentally in [5, 6] in the temperature range from 600 to 1800 K.

4. Conclusions

We have measured the widths of the rotational components of CARS spectra of the Q-branch of hydrogen molecules at a temperature of 2700 K at water-vapour densities from 1 to 4 amagat under conditions when they are determined mainly by collisions of hydrogen molecules with water molecules. The line profiles were analysed by the CARS technique. The CARS spectra for an individual rotational line were investigated with the help of a Fabry–Perot interferometer and a multichannel photodetector. The temperature was measured an additional broadband CARS spectrometer.

The broadening coefficients obtained by us are in good agreement with the data presented in [5–7], where measurements were made at lower temperatures and under lower pressures.

Measurements at such high temperatures and pressures were made possible due to the use of a specially developed pulse H_2-O_2 combustion chamber. The diagnostic and measuring complex designed by us allowed synchronous measurements of the widths of spectral profiles, temperatures and pressures in the combustion chamber.

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